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Influence of pH Solution on the Electrodeposition of Tungsten Oxide (WO₃) Films onto Indium Tin Oxide (ITO)-glass Substrate

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Abstract

An investigation on the influence of pH solution on the formation of tungsten oxide (WO₃) films on indium tin oxide (ITO) - coated glass substrate was carried out. The films have been electrochemically deposited from bath solution containing Na₂WO₄·2H₂O and H₂O₂ at different pH values using constant potential of -0.45V vs Ag/AgCl for 300s. The surface morphology and crystalline structure of the prepared films were characterized by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD), respectively. The electrochemical behaviour of the films in 1 M HNO₃ was measured by cyclic voltammetry (CV). It was observed that the morphology and electrochemical behavior of WO₃ films strongly depend on pH value. A smooth and thin WO₃ film was deposited on ITO from pH solution of 1.30; however, the deposition at lower pH value (i.e.: pH=0.80) under the same electrodeposition conditions has produced a porous and thick film. The porous film has greatly enhanced the electrochemical behaviour of WO₃ for intercalation and de-intercalation of H⁺ ions due to its high surface area.

Keywords: electrodeposition; tungsten oxide; indium tin oxide; electrochromism

1. INTRODUCTION

In recent years, tungsten oxide (WO_3) film has been a material of rapidly growing attention of researchers due to its interesting properties such as electrochromism, optical and electrical [1,2,3,4]. It is widely used in many technological applications; for example in chemical sensors [5], electrochromic devices [6], smart windows [7] catalysis and solar cells [8].

Many reports published on WO_3 films lead to the conclusion that the film properties are strongly influenced by deposition solutions, conditions and techniques. There are several precursor solutions can be used to produce WO_3 films based on the following materials such as tungsten powder [9], WOCl_4 [10], $\text{W}_2[\text{OC}(\text{CH}_3)_3]_6$ [11] and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ [4]. The films can be prepared onto substrates by a variety of techniques, such as vacuum techniques (sputtering [8], thermal evaporation [12] and chemical vapor deposition [13]) and chemical methods (spin coating [14], spray pyrolysis [15], sol-gel deposition [10,11,16] and electrochemical deposition [4,9,17]). The electrochemical deposition has advantages as compared to other preparation techniques because of its simplicity, low equipment cost, feasibility of room temperature growth and the possibility in producing large area films [18]. Furthermore, this technique can generate desirable films by modifying experimental solutions and conditions.

This study aimed at studying the electrodeposition of WO_3 films on transparent conducting optically glass (i.e.: indium tin oxide (ITO) coated glass) from different pH solutions containing tungstic acid. The effect of the deposition solutions on the morphology, structure and electrochemical behavior of the resulting WO_3 films will be discussed. The formation of good quality WO_3 films is very important in the production of electrochromic devices especially for smart windows application.

2. EXPERIMENTAL

A conventional three-electrode cell was used in the deposition of WO_3 films with indium tin oxide (ITO)-coated glass (sheet resistance $\sim 20 \Omega/\text{cm}$) substrate as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode. The bath solution consisted of aqueous tungstic acid containing 0.05M $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O} + 5 \text{ mL } \text{H}_2\text{O}_2$ and pH was adjusted by adding HNO_3 . Analytical grade reagents were used in all preparation. The pH value of bath solution was measured with a precise pH meter (Mettler Toledo Ross FE20). Prior to film deposition, the ITO substrates were cleaned with detergent and diluted hydrochloric acid and were then rinsed with ethanol and distilled water.

Electrodeposition processes were carried out under potentiostatic condition using Autolab Potentiostat Model AUTOLAB (AUTO302N.FRA2). A constant potential of -0.45V vs Ag/AgCl was applied for all WO₃ films deposition for 300s at ambient temperature (25 ± 2 °C). After deposition, the specimens were rinsed with de-ionized water to remove residual electrolyte.

The surface morphology of the films was observed by CARL ZEISS SMT SUPRA 40VP field emission scanning electron microscopy (FESEM). The crystalline structure of the ITO (blank) and WO₃ films was measured by XRD instrument X'PERT PRO – MPD (with Cu K α radiation) with the range from 20° – 70° at 2 θ . The electrochemical properties of the films were characterized by cyclic voltammetry measurements. The experiments were carried out in a standard three-electrode instrument using Platinum (Pt) as counter electrode and silver/silver chloride (Ag/AgCl) as reference electrode. The electrolyte was 1 M HNO₃ solution. The data were recorded directly by a computer.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of WO₃ Films

A series of experiments using cyclic voltammetry was carried out to define the influence of pH of bath solution on the deposition and dissolution of WO₃ on/from ITO substrate. The voltammograms were recorded from +0.2 to -1.0 V and scanned back to 0.0 V by scanning the potential at a scan rate of 50 mV s⁻¹. All the potentials are quoted versus Ag/AgCl.

Figure 1 shows the overlays of three cyclic voltammograms (CV) produced from the deposition and dissolution processes of WO₃ at three different pH solutions (ie: 0.80, 1.30 and 1.80) containing 0.05 M Na₂WO₄.2H₂O + 5 mL H₂O₂.

Cyclic voltammogram produced from pH 1.80 solution (see Fig. 1a) shows a rapid increase in current starting from E = -0.1 V on the cathodic scan until -0.7 V corresponds to the formation of WO₃ film through the reduction process believed to be W⁶⁺ to W⁵⁺. An additional curve after -0.7 V to -1.0 V represents the evolution of H₂ bubbles through the following electrochemical reaction as in Equation [1]:



Meanwhile, for CV produced from pH 1.30 solution (see Fig. 1b), there are two curves present on the cathodic scan before the production of H₂ (i.e.: E < -0.7 V). A probable explanation for these two curves is the reduction of two types of tungsten ions (i.e.: W⁶⁺ and W⁵⁺) present in the bath solution. As can be seen in the figure, the first curve starting from -0.1 V to -0.4 V is believed to be the reduction of W⁶⁺ to

W^{5+} and the second curve from -0.4 V to -0.7 V is probably due to the reduction of W^{5+} to W^{4+} . Further experimental work is necessary for definitive peaks determination. As reported earlier by J.N.Yao *et al.* [4], XPS spectra of WO_3 films prepared from $Na_2WO_4 \cdot 2H_2O$ aqueous electrolytes showed evidence for tungsten in different valence states, W^{4+} , W^{5+} and W^{6+} .

However, by decreasing the pH value to 0.80, the coagulation of WO_x particles to form colloidal suspension has shifted the cathodic reduction potential of tungstate ion to more positive potential (i.e.: $E = +0.2$ V). It is clearly seen that the current for the deposition and dissolution of WO_3 as well as the H_2 evolution process is much greater at pH 0.80 than higher pH solutions. This is believed to be due to the presence of higher amount of H^+ ions and the presence of WO_x particles close to the cathode surface. These factors have also enhanced the deposition rate of WO_3 film.

Prior to each deposition, freshly prepared bath solutions must be used in order to get a reproducible WO_3 films and cyclic voltammograms. This is due to the instability of the bath solutions with respect to storage time. Aqueous solutions of tungstic acid (H_2WO_4) are not stable due to hydrolysis of H_2O_2 and, consequently, rapid condensation and precipitations occurs if the solutions are not stabilized. Therefore, the storage time of each solution must be taken into account in order to produce reproducibility of results. G. Leftheriotis and P. Yianoulis [19] have reported that the morphology and properties of WO_3 films deposited immediately after the solution preparation are totally different than films deposited from the same solution after being kept for two or more days due to the formation of conglomerations within the bath solution.

Table 1 summarizes the characteristics of deposition solutions containing tungstate ion at different pH values and the WO_3 films formed on ITO as observed by FESEM. The pH value was adjusted by adding various amounts of nitric acid. Before adding nitric acid, the original pH solution containing only 0.05 M tungstate ion and 5 mL H_2O_2 was 9.90. It was found that the deposition of WO_3 film onto the ITO substrate from this pH solution was impossible due to the formation of a lot of bubbles at the ITO surface during the deposition process.

Table 1: Characteristics of deposition solution containing 0.05 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ + 5 mL H_2O_2 with the presence of different amount of nitric acid; and WO_3 films formed after 300s deposition at -0.45 V and the resultant films as observed by FESEM.

Solution pH	Color	Solution appearance	WO_3 films formed as observed by FESEM
1.80	Very Light Yellow	No colour change	Only a few particles of WO_3 deposited
1.30	Light Yellow	Fine and small particles of WO_3 in the solution	All surface covered, smooth and thin film
0.80	Milky yellow	Colloidal suspension, the formation of yellow sediment at the bottom of container if left unstirred	All surface covered, porous and thick film

The addition of HNO_3 has brought down the pH values to acidic conditions. At pH 1.80, the bath solution was in very light yellow and appeared to be stable for a period of time. A small current was recorded flowing during the deposition ($\sim -0.5 \text{ mA cm}^{-2}$) which similar to the CV shown in Fig. 1a at potential -0.45 V. It was found that the electrodeposition for 300 s was not sufficient for WO_3 to form deposits on the ITO surface. It is believed that, at this length of time, only nucleation of WO_3 occurred and there was no growth of WO_3 film as observed by FESEM. A smooth blue colour of tungsten bronze (H_xWO_3) layer was observed on the ITO surface during deposition process but no WO_3 film was observed formed on the ITO after the process. This is due to the WO_x particles only formed near the ITO (cathode) surface during the deposition process as observed by the blue colour but not deposited on the substrate.

However, when the pH value of the bath solution was decreased to 1.30, a smooth thin film of WO_3 was formed as the result of the deposition. From the CV in Fig. 1b, the current density recorded for the deposition at -0.45 V was -1.0 mA cm^{-2} , which was double to the deposition at pH 1.80. The higher current density used for the deposition has produced a complete layer of WO_3 film on the entire ITO surface. The morphology of the resultant film will be discussed in the next section. At pH 1.30, the bath solution was found to be stable and no precipitation of tungstate particles at the bottom of the flask after left standing for a few days.

When the pH solution was further decreased to 0.80, a colloidal solution was formed and the colour of the solution turned to milky yellow (arising due to particle coagulation). The colloidal solution was not stable and if left unstirred the precipitation of yellow sediment was found at the bottom of the container after one day. From CV in Fig. 1c, at -0.45V, the current density observed was -2.2 mA cm^{-2} which at steady state of the reduction process. High current density contributes to

high deposition rate. A deep blue colour was observed on the ITO surface during the electrodeposition of the WO_3 film and the colour vanished almost immediately after its removal from the bath solution. The resultant film was thick and porous as observed by the naked eye and FESEM.

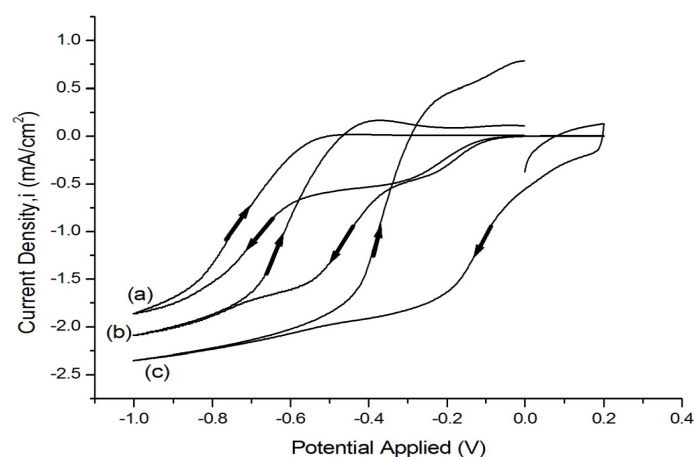


Figure 1: Overlays of cyclic voltammograms of ITO-glass electrode in nitric acid solutions at (a) pH 1.80 (b) pH 1.30 and (c) pH 0.80, containing 0.05 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}_2$ at scan rate 50 mV s^{-1} .

3.2 Morphological and Structural Analysis

The morphologies of ITO surface (blank) and all WO_3 films prepared onto ITO substrates from solution containing tungstate ions at three different pH values were observed and recorded by FESEM. Fig. 2a shows SEM image of ITO substrate used in this study in which the morphology appears to have irregularities of small grains and fibril like shape structure with various sizes, ranging from 10 nm to 100 nm. The substrate appears very uniform and highly transparent to the naked eye.

The electrodeposition of WO_3 film onto ITO substrate from pH solution of 1.80 at -0.45 V for 300s resulted an image as seen in Fig. 2b. In the figure, the presence of a few WO_3 crystals (in circles) on the ITO surface was observed by FESEM. It is believed that the deposition at -0.45 V with a very low current density (i.e.: -0.5 mA cm^{-2}), as indicated by CV in Fig. 1a, only involved the nucleation of WO_3 particles but no growth of the film.

However at pH=1.30, under the same electrodeposition conditions, the resultant film consisted of smooth fine grains with a few cracks was observed by FESEM as shown in Fig. 2c. The film was thin and transparent to the naked eye. The outcome of this smooth film was attributed to a low current density (ie: -1.0 mA

cm^2) applied during the deposition process. The applied current density corresponds to the current density value at -0.45 V of CV as shown in Fig. 1b.

Meanwhile, preparation from solution with adjusted pH of 0.80, a very dense and porous WO_3 film with agglomerated granules was formed as shown in Fig. 2d. It is apparent that more WO_3 was deposited on ITO substrate with decreasing pH value. It is believed that the presence of a lot of tungstate particles in colloidal solution close to the cathode surface during deposition process has led to a very fast deposition of WO_3 . At the same time at low pH value, the particles of WO_x form directly on the cathode surface, migrate across the electric field and deposit on the ITO surface. The electrodeposition of WO_3 film achieved via particle coagulation is known as electrophoretic deposition. Furthermore, at pH 0.80, the deposition process carried out at -0.45 V is totally controlled by mass transport process (steady state region) with high current density of -2.2 mA cm^{-2} as indicated by cyclic voltammetry shown in Fig. 1c.

The faster nucleation and growth of WO_3 from pH solution of 0.80 were indicated by the production of a thicker and denser film as compared to deposition at higher pH values. It was found that the pH of the deposition solution plays a very critical role in tailoring the surface morphology of the WO_3 films. By increasing the concentration of acid in the deposition solution, the WO_3 film was easily deposited onto ITO surface. According to B. Yang *et al* [9], low density mesoporous WO_3 films can be prepared from pH 0.80 solution containing dissolved tungsten powder in H_2O_2 and H_2SO_4 using cyclic voltammetry scanned from -0.8 V to +0.2 V for three cycles or using constant cathodic current density of -0.4 or -0.8 mA cm^{-2} for 10 min or 5 min. This shows that a similar finding of porous WO_3 film as in this study was observed and reported by other researchers for deposition from pH solution of 0.80 although they were using different starting materials and different deposition methods.

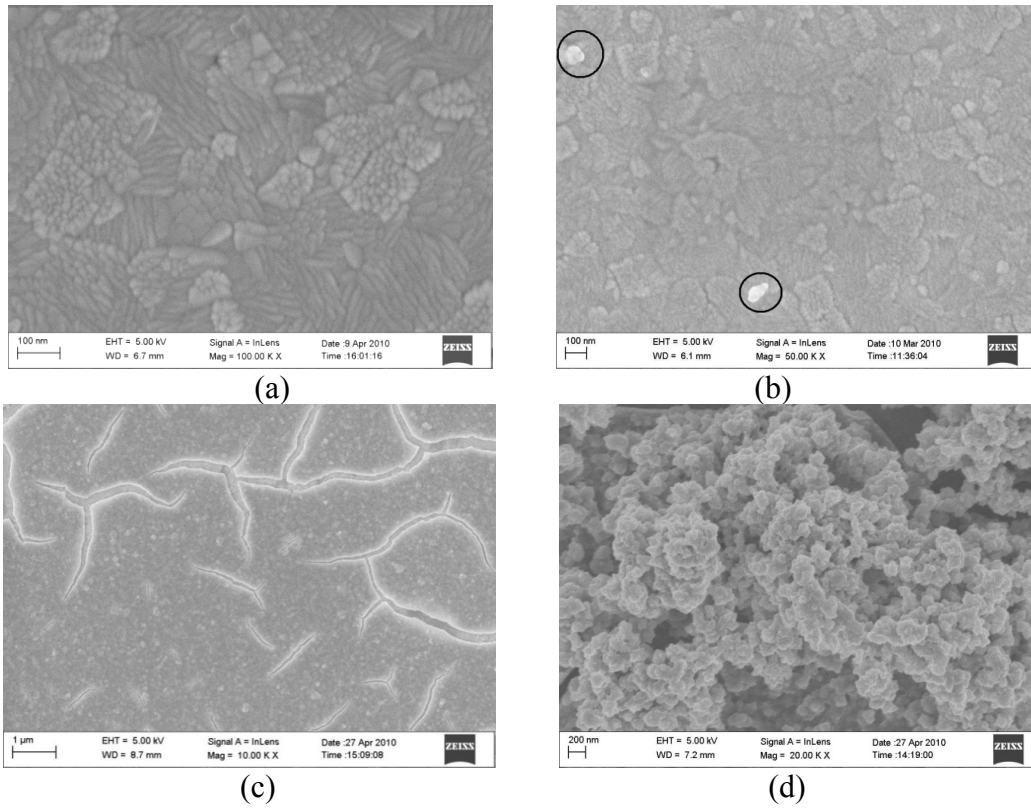


Figure 2: SEM images of (a) ITO-glass substrate (b) WO₃ film deposited at pH 1.80 and (c) WO₃ film deposited at pH 1.30 and (d) WO₃ film deposited at pH 0.80.

X-ray powder diffraction (XRD) patterns of blank ITO and as-deposited WO₃ film (i.e.: porous) prepared at pH = 0.80 are illustrated in Figure 3. The comparison of the diffraction patterns shows the presence of a broad peak at the angle of $2\theta = 26^\circ$ for the porous film which corresponding to the formation of amorphous film of WO₃. It was also found that the intensity of the diffractogram peaks of ITO for the as-deposited film was also decreased. This indicates that the ITO substrate was covered with a layer of WO₃ film.

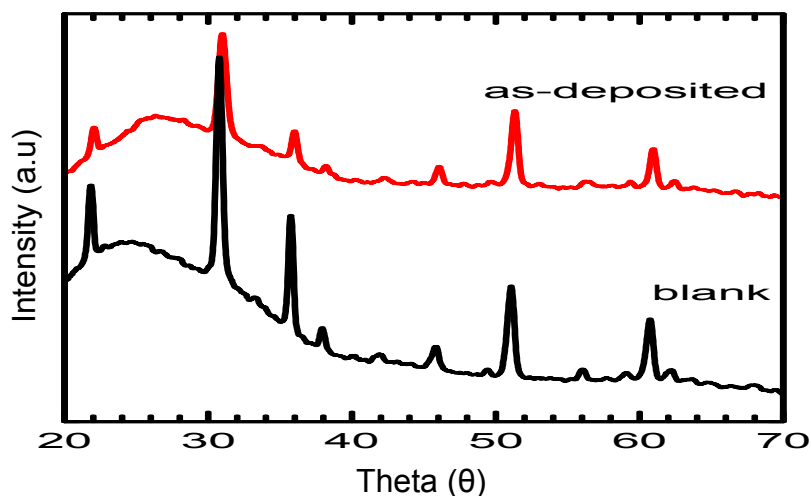


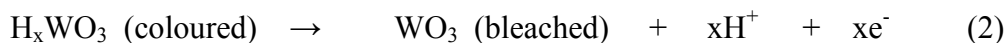
Figure 3: Comparison of XRD patterns of blank ITO and as-deposited WO₃ film prepared at pH=0.80.

3.3 Electrochemical Behaviour of WO₃ Films in 1M HNO₃

WO₃ films deposited from pH 0.80 and pH 1.30 solutions present an interesting comparison. Both films were grown from the same deposition conditions except the pH of the deposition solution. Clearly, the resultant WO₃ film prepared from pH 0.80 solution is much thicker with highly porous than the smooth film prepared from pH 1.30 as shown earlier in SEM images (see Fig. 2c and 2d).

To make a further comparison, we have investigated the electrochemical behaviour of both films in nitric acid. Figure 4 shows cyclic voltammetric responses for both WO₃ films, prepared from pH 1.30 and pH 0.80 solutions, in 1M HNO₃. The applied potential was varied between +0.6 V and -0.6 V (intercalation) and back to +0.6 V (de-intercalation) at a scan rate of 50 mV s⁻¹.

The current density recorded is due to a proton (ie: H⁺) intercalation (coloration) / de-intercalation (bleaching) according to the electrochemical reaction as follows:



where H⁺ is hydrogen ion in 1M HNO₃.

It was found that the porous WO₃ film with agglomerated granules has produced much greater current density for both intercalation and de-intercalation processes than that of the smooth film. The porous film also produced more intense blue colour during intercalation of H⁺ ions as compared to the smooth film which

producing light blue colour. The difference in colour intensity is due to the higher surface area available for the proton ions to intercalate into the porous WO_3 film prepared from pH 0.80 solution as compared to the smooth film deposited from pH 1.30 solution.

The diffusion coefficient of H^+ ions (D) during intercalation and de-intercalation for the porous WO_3 film was calculated from the Randles-Servcik equation :

$$D^{\frac{1}{2}} = \frac{ip}{2.72 \times 10^5 \times n^{\frac{3}{2}} \times C_o \times v^{\frac{1}{2}}} \quad (3)$$

where ip is the peak current density (anodic peak current ip_a , and cathodic peak current, ip_c), n is the number of electrons transfer (assumed to be 1), C_o is the concentration in bulk and v is the scan rate.

The calculated values of D for intercalation and de-intercalation of H^+ ions to and from the smooth WO_3 film (prepared in pH=1.30) were $8.68 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ and $6.93 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, respectively. Meanwhile, the D values of H^+ ions intercalation and de-intercalation at the porous WO_3 film were $1.02 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $9.18 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, respectively. This clearly indicates that the porous WO_3 film permits more H^+ ions to diffuse from the electrolyte into the WO_3 electrode than the smooth film. The porous film exhibits a better electrochemical performance than the smooth film due to the fact that it has a more surface area. This porous film is a very promising for electrochromic applications, provided that it exhibits good cycling stability and fast switching rate from coloured to bleached states. The study of stability and switching rate of WO_3 films will be the subject of a forthcoming paper.

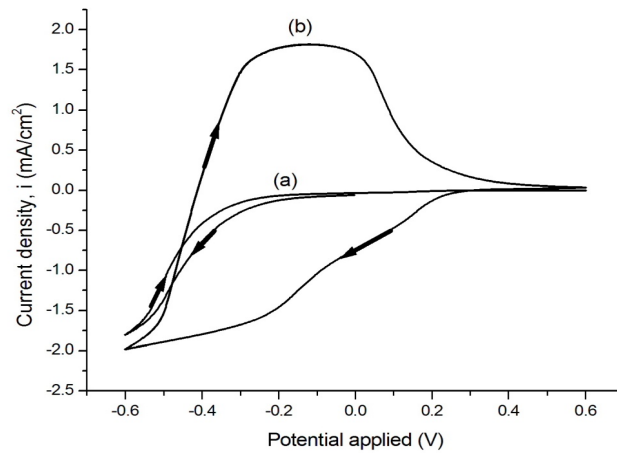


Figure 4: WO_3 films deposited at (a) pH 1.30 and (b) pH 0.80 in bleached and coloured states by intercalation and deintercalation of H^+ ions.

4. CONCLUSIONS

The electrodeposition of WO₃ films is strongly dependent on the pH of the deposition solution. It was observed that the pH value of the solution played an important role in modifying the surface morphology of the films. The nucleation density and growth rate of WO₃ increased with decreasing pH values (high H⁺ concentration) and also the presence of colloidal particles close to the cathode surface has enhanced the deposition rate of WO₃ films. The resultant WO₃ film prepared from a pH solution of 0.80 showed a greater performance for the intercalation/de-intercalation of hydrogen ions as compared to WO₃ film prepared in pH=1.30, with H⁺ ion diffusion coefficient values as high as $1.02 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The porous film exhibits promising electrochromic coloration properties for smart window applications.

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